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# Introduction: minerals to MOFs

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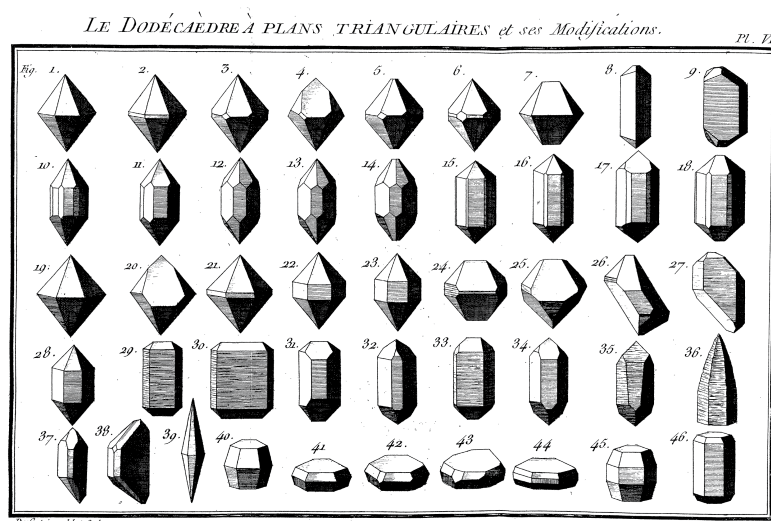
Mineralogy and materials design have always been closely intertwined. Here I review some of the earliest work in modern materials chemistry to explicitly take inspiration from mineral structures and properties, and introduce the invited contributions to this Theme Issue.

The discipline of mineralogy is as old as science itself, going back to the earliest prehistoric investigations of minerals' appearance and behaviour. It is only natural, therefore, that scientists who create synthetic materials should look to minerals for inspiration.

On one hand, we might be motivated by minerals' properties. People have always been fascinated by gemstones' beauty, of course; but the search for what we would now call functional materials also has ancient roots. The Greek philosopher Theophrastus, for instance, in his monograph *On Stones* (4th century BCE), classifies amber, "lyngourion" (probably tourmaline [1]), and the "Heracleian stone" (lodestone) together, since they are all materials with "the power of attraction" [2]. In modern language, we say that amber's attractive power arises from triboelectricity and tourmaline's from pyroelectricity, while magnetite's is due to ferrimagnetism. Theophrastus' work, then, is a very early description of materials valued for their electric and magnetic functionality.

On the other hand, we can attempt to mimic minerals' structure. In early work, this meant the macroscopic structure (Figure 1), although crystallographers were well aware that this must be a reflection of a microscopic structure that was to them undetectable. Later, the focus shifted to similarities at the atomic scale, with the development of new materials with the same geometric or topological structure as known minerals.

Of course, these two forms of mimesis are most relevant where they occur together. If we can isolate a structural origin for some property of a mineral – its functionality, or the way it is formed or degrades in nature – we might hope to build upon that understanding, modifying the structure in such a way as to improve or even tune its behaviour. This broad research aim underlies some of the most exciting work in the modern chemistry and physics of materials, including the research



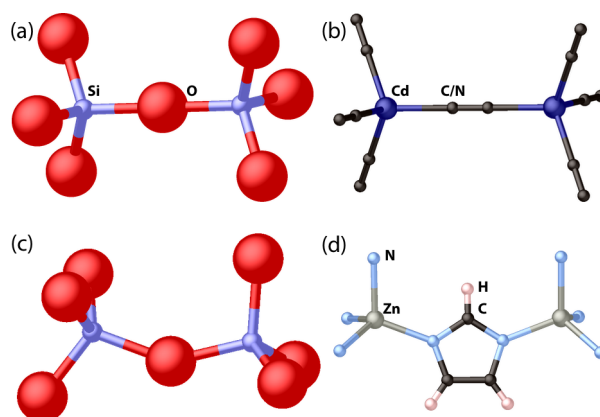
**Figure 1.** Variations on the theme of a triangular-faced dodecahedron (hexagonal bipyramid), as presented in Jean-Baptiste Louis Romé de l'Isle's treatise *Crystallographie*, 1783.

highlighted in this Theme Issue.

The word “mineralomimesis” itself was first brought to prominence in the chemical literature by Toschitake Iwamoto, Shin-Ichi Nishikiori, and Takafumi Kitazawa in the 1990s. These scientists pointed out that tetrahedral complexes of  $d^{10}$  metals – in particular  $\text{Cd}(\text{CN})_4$  units – share a topology with the tetrahedral  $\text{SiO}_4$  units that make up the silicate minerals [3,4]. This immediately proved to be a fruitful analogy: inclusion compounds of  $\text{Cd}(\text{CN})_2$  and other cyanometallates rival the silicates themselves in structural variety. In fact, these compounds, with linear  $\text{Cd}-\text{C}\equiv\text{N}-\text{Cd}$  chains, mimic specifically the average structure of  $\beta$ -cristobalite, with a linear  $\text{Si}-\text{O}-\text{Si}$  linkage (Figure 2a, b). Later, the zeolitic imidazolate frameworks (ZIFs) were developed, again with silicates in mind, but this time with more realistically bent links (Figure 2c, d) [5]. Again, this analogy proved immensely profitable, with the subsequent development of ZIF structures analogous not only to the silicate zeolites but also to amorphous and even liquid silica [6,7].

At the same time, inorganic chemists had been developing new ways of designing materials with specific framework topologies in mind. In prescient work, Bernard Hoskins and Richard Robson demonstrated that the diamond topology could be deliberately targeted using combinations of the same tetrahedral  $d^{10}$  coordination sites and rigid linear or tetrahedral organic ligands [8,9]. These ideas were further developed by Michael O’Keefe and Omar Yaghi into the concept of reticular chemistry, which decoupled framework topology from the specific geometry or chemistry of any particular material. In particular, this introduced the possibility of isorectical series in which the linker size could be systematically varied while the topology remained constant [10]. Metal-organic frameworks (MOFs) and related coordination polymers are now often described in terms of their topology. Developments such as the freely available Reticular Chemistry Structure Database [11] and ToposPro (previously Topos) software [12] have made topological analysis a widely used component in any crystallographer or crystal engineer’s toolkit.

In the past decade, the most dramatic development in mineralomimetic chemistry has been the rapid rise of interest in the “hybrid perovskites”. The lead halide materials, and related compounds such as tin- or bismuth-containing analogues, have rightly attracted enormous attention for their promising optoelectronic properties [13]. However, the family extends far beyond these [14,15]. While materials in this family have been known as far back as the 1970s [16], the analogy to the perovskite structure was to my knowledge first pointed out by Song Gao and co-workers in



**Figure 2.** Mimicking silicate tetrahedra: (a) the spatial average  $\beta$ -cristobalite structure, showing an  $180^\circ$  linkage between two  $\text{SiO}_4$  tetrahedra, is topologically equivalent to (b) the cyanide-bridge linkage between  $\text{Cd}(\text{C/N})_4$  tetrahedra in cadmium cyanide. (c) The true  $\text{Si}-\text{O}-\text{Si}$  angle, as seen in  $\alpha$ -cristobalite and in the *local* structure of  $\beta$ -cristobalite, is closer to  $145^\circ$ ; this is mimicked by (d) the imidazolate linkers in the zeolitic imidazolate frameworks.

2004 [17]. Subsequent work has excitingly shown that this analogy extends beyond topology: like their inorganic counterparts, the hybrid perovskites have important magnetic [18] and electric properties [19,20]. (Incidentally, the most abundant mineral in the Earth's mantle is bridgmanite, a silicate with the perovskite structure; thus, although of course perovskite itself is not a silicate, the family of hybrid perovskites represents another example of synthetic materials mimicking a silicate phase.) Highlighting early work on the formate perovskites among other materials, Cheetham and C. N. R. Rao made the perceptive comment that there's "room in the middle" [21] – that is, that the chemistry and physics of coordination frameworks opened unique possibilities, not available in the world of purely inorganic or organic materials, that deserved further investigation. Twelve years later, this is truer than ever, as the work showcased in this Theme Issue amply demonstrates.

We begin the issue with fundamental questions from the experimental and computational points of view: how do we make a mineralomimetic framework in real life or *in silico*? Igor Huskić and Tomislav Friščić remind us some minerals can themselves be considered MOFs, using the natural processes by which these are formed and degrade as inspiration for environmentally friendly preparations of synthetic analogues [?]. Guillaume Fraux, Siwar Chibani and François-Xavier Coudert emphasise the importance of multiscale modelling to give a realistic computational picture of these materials, and review the use of materials databases, machine learning, and other big-data methods that are increasingly prominent ways to develop these models [?].

The second section of the issue focuses on atomic and magnetic structure. The articles on atomic structure emphasise the new possibilities that are unlocked when atomic ions in mineral structures are replaced by organic molecular ions. Andrew Goodwin and co-workers demonstrate how these ions' intrinsic quadrupole or octopole moments may lead to unconventional ferroic order-disorder transitions [?]. My own group's contribution to the issue is an example of a phase transition under pressure, illustrating how host-guest hydrogen bonding – a unique feature in coordination frameworks compared to their mineral analogues – can stabilise particular crystallographic structures [?]. The articles from the groups of Lucy Clark [?] and of Paul Saines [?] both consider magnetic frustration in different framework topologies. Magnetic exchange is among the subtlest and most variable features of coordination frameworks, and these articles demonstrate the variety of magnetic order and disorder that can be achieved even in apparently analogous materials.

The third and final section deals with atomic and electrical dynamics. This section opens with a personal perspective from Martin Dove on the concept of flexibility [?]. His rigid unit mode model is yet another example of a successful transplant from the world of silicates to coordination

frameworks; the perspective corrects some misconceptions in the way it has been applied, and illustrates the consequences of flexibility in mineralomimetic frameworks. Elise Miner and Mircea Dincă review the application of MOFs and their close relatives the covalent organic frameworks (COFs) in solid-state electrolytes, discussing structural routes to ionic conductivity [?]. By contrast, the review by Deanna D'Alessandro and co-workers considers the origins and uses of electrical conductivity and redox activity in these materials [?].

Despite the diversity of these articles, I can make no claim that this theme issue is in any way comprehensive. Rather, I hope that it will serve as a snapshot of some of the important properties and applications of mineralomimetic frameworks and the deeper questions in materials chemistry and physics they help to illuminate; and that it may even contribute to stimulating further interest in this vast and fascinating subject.

It is a great pleasure to thank all of the authors for their contributions to this Theme Issue and good humour through the process of assembling it; Rebecca Lingwood (Brunel University) for commissioning the issue; and Bailey Fallon (The Royal Society) for shepherding it through to publication.

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